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7/25/68

CORROSION CHARACTERISTICS OF DENTAL AMALGAM

A THESIS

Presented to

The Faculty of the Graduate Division

by

Larry Dennis Love

In Partial Fulfillment

of the Requirements for the Degree

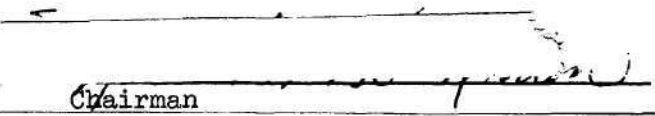
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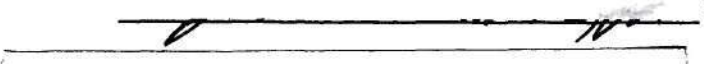
Georgia Institute of Technology

July, 1970

CORROSION CHARACTERISTICS OF DENTAL AMALGAM

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## SUMMARY

This study was undertaken to determine the corrosion tendency and characteristics of dental amalgam in artificial saliva. Electrochemical measurements were made by normal potentiostatic methods to investigate a possible active-passive transition. The amalgam surfaces were studied using standard metallographic and electron microprobe techniques.

The results showed that amalgam does undergo an active-passive transition and that the corrosive process initiates in surface defects. Tin was found to be corroded preferentially to silver. The corrosive resistance of amalgam can be attributed to factors other than the establishment of a passive surface film. The electrical potential and current density required to promote an active-passive transition in dental amalgam are greater than those which occur in the oral cavity. Therefore, the good corrosive properties of amalgam in situ are attributed to the high circuit resistance in an oral environment and to amalgam being a relatively noble material.

## CHAPTER I

### INTRODUCTION

Electrical phenomena in the human oral cavity have been described and reviewed in many papers published between 1878 and the present (1). The earlier papers were concerned primarily in determining if the electrolytic action between dissimilar metals and alloys which are used for dental fillings and prosthetic appliances was responsible for certain symptoms that can be observed in the mouth. It was thought that electrical currents flow between different metals and that this current was the cause of soft tissue irritations and certain pathological conditions such as leukoplakia and oral cancer (2-6). Cases were described in which the soft tissue irritation was eliminated when the metallic restorations were removed or replaced so that all metallic restorations were of the same type metal or alloy. Other clinical investigations found no differences in the oral soft tissue in the presence of dissimilar metals (2, 7-9).

Corrosion and tarnish are other undesirable features of metallic dental restorations. It has been reported that corrosion of restorations results partially from galvanic currents generated between dissimilar metals (2, 10). Farrell (11) has reported potential differences between gold and amalgam restorations, with saliva serving as the electrolyte, to be as high as 500 millivolts and that the potential difference is sufficient to induce current flow and therefore electrochemical corrosion.

Schiever and Diamond (1) described three possibilities as the source of electric current which exist in a mouth containing two or more metallic fillings. The first type of cell is produced by two metallic fillings, one gold and one amalgam for example, and the saliva which acts as the electrolyte. This type of cell is referred to as a dissimilar electrode cell. Another possible cell is produced in these same two fillings because the fillings contact the bone fluid through the teeth. Bone fluid is a term that has been used to describe the dentin, soft tissue, and blood which provide a means for completing the external circuit. It also serves as an electrolyte, thus another dissimilar electrode cell is produced. The third possible cell described by Schriever and Diamond was a liquid-junction cell formed by a single filling. This cell is illustrated in Figure 1. The single filling contacts both bone fluid and saliva which are in contact through tissues and the requirements for another cell are met.

Corrosion of amalgams has also been attributed to its inherent structural inhomogeneties. The dental amalgam has at least three different phases in contact with each other and exposed to the oral environment. The three phases forming the dental amalgam are  $\gamma(\text{Ag}_3\text{Sn})$ ,  $\gamma_1(\text{Ag}_2\text{Hg}_3)$ , and  $\gamma_2(\text{Sn}_8\text{Hg})$ . The phases containing tin have the most active potentials with  $\gamma_2$  being the most active (12).

It is possible to have the necessary conditions to cause concentration cell corrosion which is a result of a variation in the composition of the electrolyte. This variation in environment is often found in the mouth because bacterial plaques and food debris produce a change in electrolyte in their immediate vicinity. It is felt that electrolytic



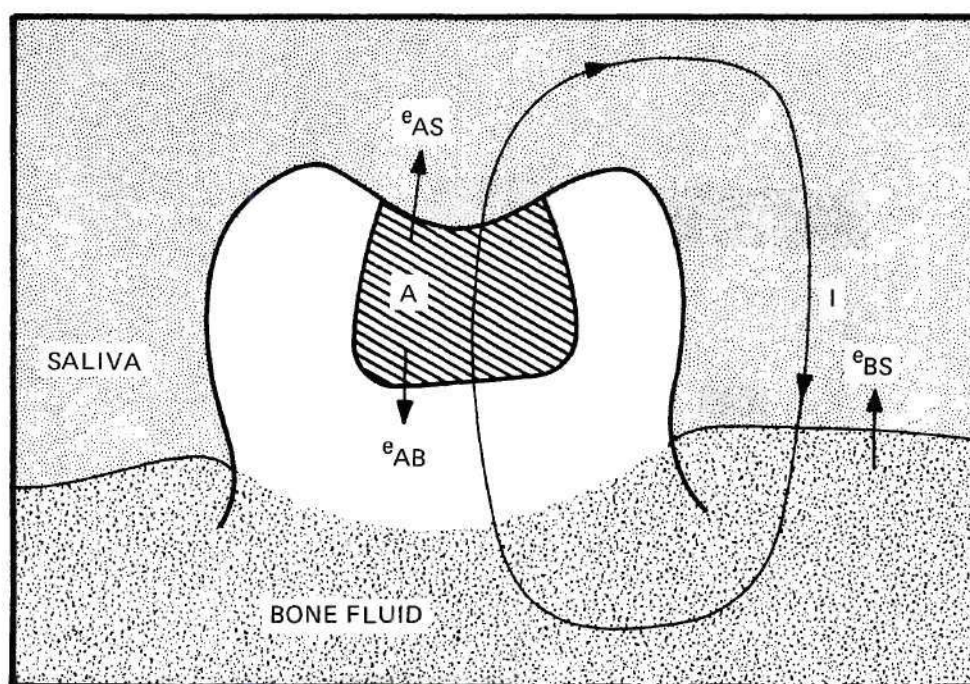


Figure 1. Liquid Junction Cell.

An Electrical Current is Produced when a Single Metallic Dental Filling is in Contact with Two Electrolytes, Saliva and Bone Fluid, which are in Contact with Themselves (1).

A, an Amalgam Filling Contacting Saliva Above and Bone Fluid Below. I, Shows the Direction of the Net e.m.f. and the Resulting Electric Current.

The Net e.m.f. in the Circuit is the Algebraic Sum of  $e_{AS}$ ,  $e_{AB}$ , and  $e_{BS}$ ; the e.m.f.'s Generated at the Metal-Saliva, Metal Bone Fluid, and Bone Fluid-Saliva Contacts.

corrosion of dental restorations generally occurs as a result of the action of the various types of corrosion cells described in the mouth.

The need for a valid corrosion test in vitro has long been recognized. In the past, the corrosion tendency of dental alloys has been assessed qualitatively by immersing the alloys in various solutions to simulate an oral environment, then noting color changes and differences in optical microscopic examination. An artificial saliva is difficult to produce because presently more than ninety constituents have been identified in human saliva (13).

In the last four years several papers concerned with the corrosion potential behavior of dental amalgam in various electrolytes have been published (12, 14-16). The recent investigators have been concerned more with developing a fundamental understanding of the corrosion mechanism in this complex alloy system while the earlier investigations dealt more with bulk dental amalgam. Carter, Ross, and Smith (14) have applied potentiostatic techniques in demonstrating the effect that various polishing agents (silicon carbide, diamond, pumice, and whiting) have on the corrosion tendency of amalgam in aerated and deaerated electrolytes. Guthrow, Johnson, and Lawless (12) also used polarization curves to show the different corrosion characteristics of amalgam and its component phases. The electrolytes used in the study were Ringer's solution and the synthetic saliva formulated by Muhler and Swenson (17).

Muller, Greener, and Crimmins (15) determined the effect of composition and processing variables by measuring the open circuit potential as a function of time. Since amalgam is a relatively noble material, they thought that conventional polarization curves would be inappropriate



in assessing the in vivo corrosion behavior of amalgam. Large currents and high potentials are necessary to produce significant passivation. They felt that normal tissue would be damaged at the potentials and currents necessary for passivation.

Lee and Greene (16) measured the corrosion potential as a function of time. The potential versus time curves were determined as a function of electrolyte and alloy composition, gaseous atmosphere, aging, and light illumination.

It is difficult to compare the results of these recent investigations concerned with the electrochemical behavior of the dental amalgam in vitro to actual in vivo deterioration. There was a great variation in the electrochemical data obtained in these studies and therefore a difference in conclusions. Potentiostatic investigations are greatly influenced by experimental techniques, especially sample preparation. All investigators did not use the same formula in preparing the synthetic saliva electrolyte nor did all amalgam test specimens have the same degree of surface polish.

Dental amalgams have relatively good corrosion resistance. The electrochemical measurements of Ross, Carter, and Smith (14) tend to indicate that amalgam exhibits an active-passive corrosion behavior and remains passive over a wide range of electrical potential. The work of Guthrow, Johnson, and Lawless (12) shows that amalgam remains passive over a much narrower range of potential and that the metal dissolution peak occurs at a more noble potential and at a relatively low current density.

Since there has been disagreement in the work of these independent

investigators, further work in this area is necessary to provide a basic understanding of the corrosion mechanism in dental amalgam. If more was known about the corrosion processes, it would aid in improving the corrosion characteristics. Noble alloy additions could perhaps improve corrosion properties if amalgam actually has an active-passive transition as is indicated by Ross and Guthrow.

### Dental Amalgam

Dental amalgam alloy refers to a class of alloy composed of silver and tin with small amounts of copper and zinc. Dental amalgam is an important alloy because it is the primary therapeutic agent in treating dental caries and is created when dental amalgam alloy is reacted with mercury. A great deal of effort has gone into developing the present composition of amalgam alloy in order to optimize the physical properties and corrosion resistance. The American Dental Association Specification for Dental Amalgam Alloys states that the alloy must contain:

Silver	65% minimum
Tin	29% maximum
Copper	6% maximum
Zinc	2% maximum
Mercury	3% maximum

The alloy is composed essentially of a silver-tin intermetallic phase ( $\text{Ag}_3\text{Sn}$ ) which is represented in Figure 2 as  $\gamma$ .  $\text{Ag}_3\text{Sn}$  is used by the dentist in the form of small irregular shaped particles or small spheres in powder form. The dental amalgam is created when  $\text{Ag}_3\text{Sn}$  is mixed with mercury in a mortar and pestle or in a mechanical amalgamator. The mixing process is referred to as trituration which initiates the chemical reaction of mercury with  $\text{Ag}_3\text{Sn}$ . An inherent protective film on the  $\text{Ag}_3\text{Sn}$  is broken during the mixing process which permits the mercury



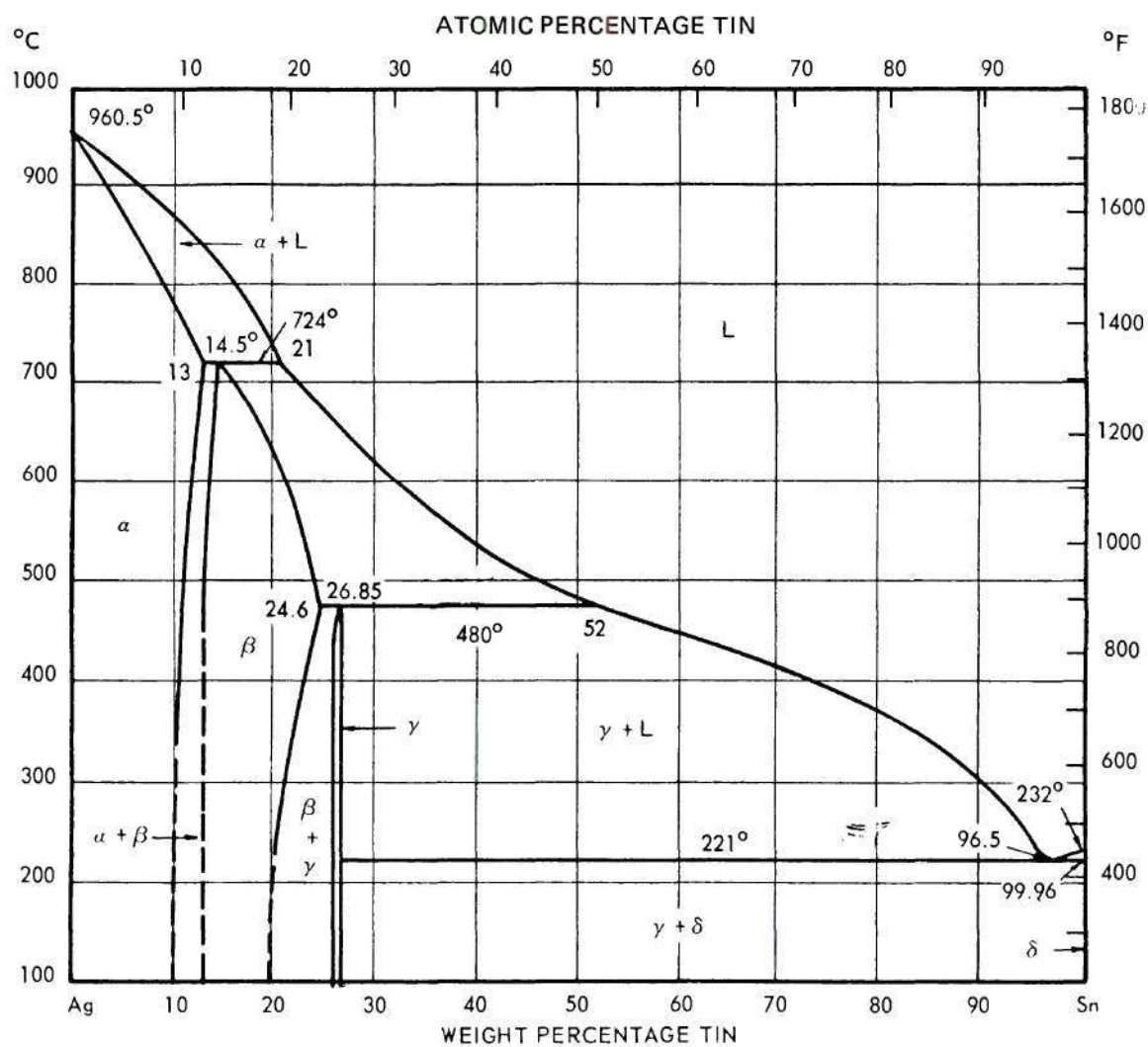
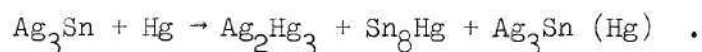


Figure 2. Silver-Tin Phase Diagram.

to wet and react with the amalgam alloy. After trituration, the excess mercury is removed by squeezing the amalgam in a cloth. The freshly mixed amalgam is in a plastic condition which permits the dentist to pack the alloy into a cavity, a process referred to as condensation.

The reaction of mercury with  $\text{Ag}_3\text{Sn}$  produces two crystalline phases, a silver-mercury phase ( $\text{Ag}_2\text{Hg}_3$ ) and a tin-mercury phase ( $\text{Sn}_8\text{Hg}$ ) that are designated  $\gamma_1$  and  $\gamma_2$ , respectively in Figures 3 and 4. The exact mechanism of nucleation and growth of the  $\gamma_1$  and  $\gamma_2$  phases when  $\text{Ag}_3\text{Sn}$  is wetted with mercury is not completely understood. It is generally believed that the  $\text{Ag}_3\text{Sn}$  absorbs mercury or the mercury dissolves the  $\text{Ag}_3\text{Sn}$  but, in either case, a solution of silver, tin, and mercury is created. The first new phase to crystallize in the solution is  $\gamma_1$  which has a body-centered cubic structure.  $\gamma_2$  having a hexagonal structure forms later than  $\gamma_1$ , but has a greater rate of crystallization. The creation of  $\gamma_1$  and  $\gamma_2$  phases continues until all of the mercury has reacted and brings about the hardening or setting of the amalgam. Koger (18) states that the completely reacted amalgam consists of unreacted  $\gamma$  particles in a matrix composed of  $\gamma_1$  and  $\gamma_2$  and the reaction can be represented as



Not much research concerned with alloy additions has been done in the last few years. However, a great deal of research devoted to manufacturing processes and manipulate techniques by the dentist has been accomplished in an effort to optimize the properties of the amalgam

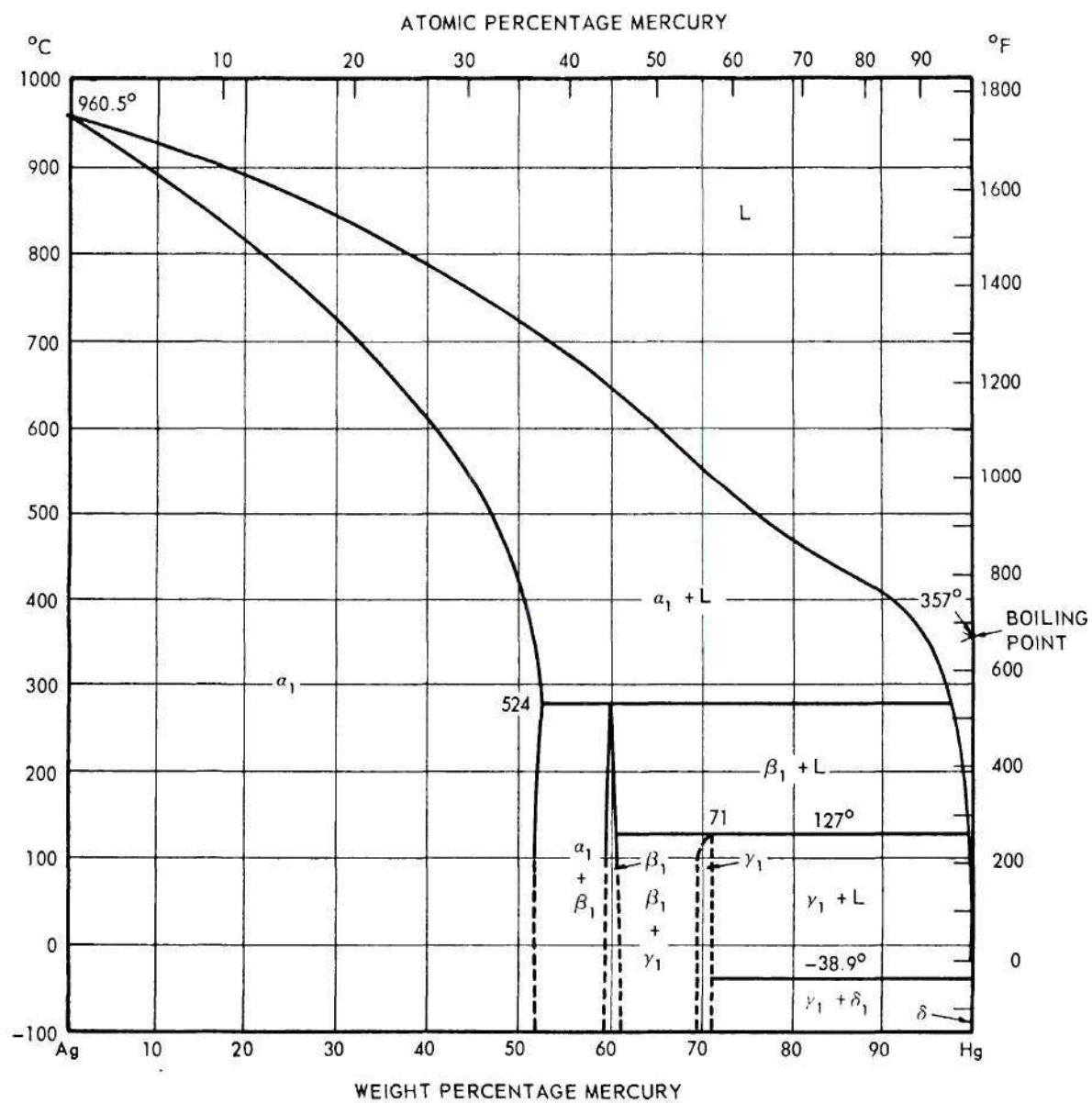


Figure 3. Silver-Mercury Phase Diagram.

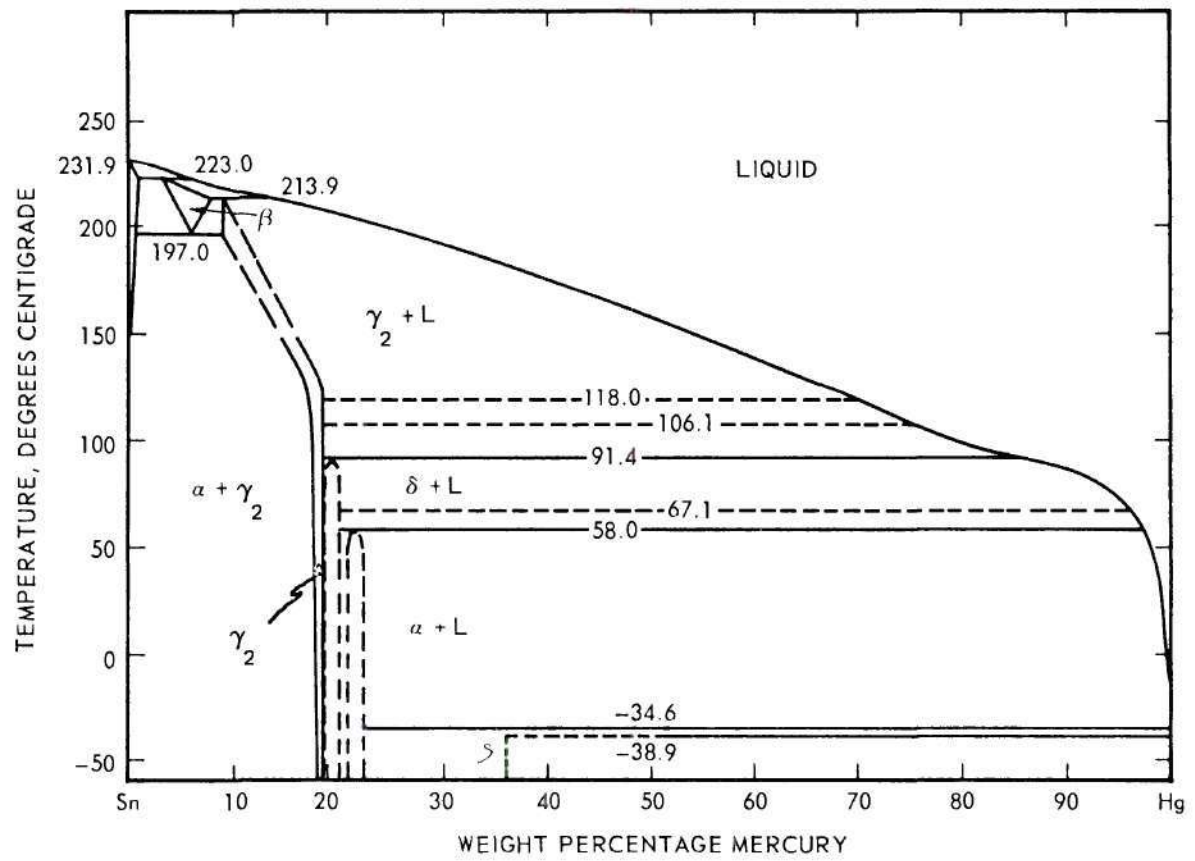


Figure 4. Tin-Mercury Phase Diagram.

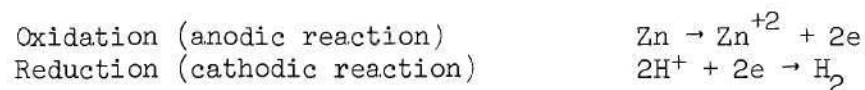


filling. From these investigations, particle size distribution and heat treatments of the amalgam alloy were developed. Also, the influence of trituration time, mercury to alloy ratio, and condensation pressure were determined.

### Electrochemical Considerations

The corrosion characteristics of a metal in an aqueous environment can be predicted from the electrochemical data provided by potentiostatic polarization methods (19). Polarization curves are determined from dynamic measurements in either of two ways. The potential may be controlled and the resultant current monitored (potentiostatic) or the current can be altered while the potential is monitored (galvanostatic). The potentiostatic method is most commonly used because the potential is easy to control and the measured current indicates the reaction or corrosion rate of the metal.

When a metal is exposed to a corrosive media, two reactions occur on its surface. There must always be at least one oxidation reaction and one reduction reaction. For example, when Zinc is dissolved by an acid, the two reactions are:



The open circuit potential (no current flow through the metal) of the metal specimen in an aqueous media is the difference between the standard electrode potential of the metal electrode ( $E_O^a$ ) and that of cathodic reactant ( $E_O^c$ ). The corrosion potential,  $E_{\text{corr}}$ , and corrosion current,  $i_{\text{corr}}$ , are shown in Figure 5 and are determined by the point of intersection of the cathodic and anodic polarization curves.

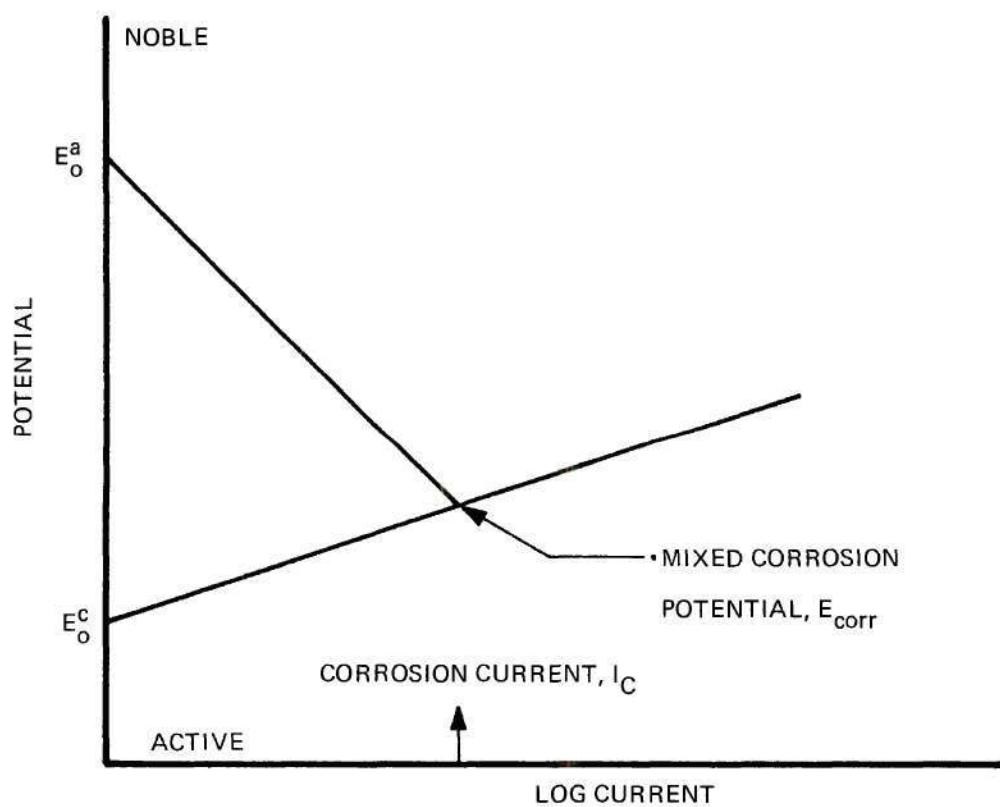
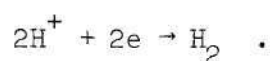


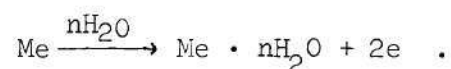
Figure 5. Schematic Polarization Curves for an Anodic and Cathodic Reaction on a Corroding Specimen which is Anodically Polarized. (From Scully 21 , Modified.)

The characteristic features of an anodic polarization curve of a metal which has an active-passive corrosion behavior are shown in Figure 6. The curve can be divided into three different regions: active, passive, and transpassive. When the metal is polarized in the negative direction from the open circuit potential, hydrogen is evolved on the metal surface by the cathodic reaction

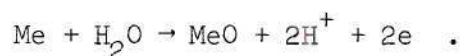


At potentials more positive than the open circuit potential, the dissolution rate of the metal increases up to the primary passive potential,  $E_{pp}$ , and the corresponding current density at  $E_{pp}$  is designated  $I_c$  in Figure 6 and is the critical current density for passivity.

Metal dissolution in the active state can be expressed by the reaction (20)



At some potential slightly negative to  $E_{pp}$ , the electrochemical production of a protective oxide film is thermodynamically possible. As the potential is increased in the noble direction from point  $\frac{E_{me}}{E_{meox}}$ , the potential at which the oxide film or absorbed layer is in equilibrium with the metal, the film layer tends to grow on the metal surface by a reaction of the type (20)





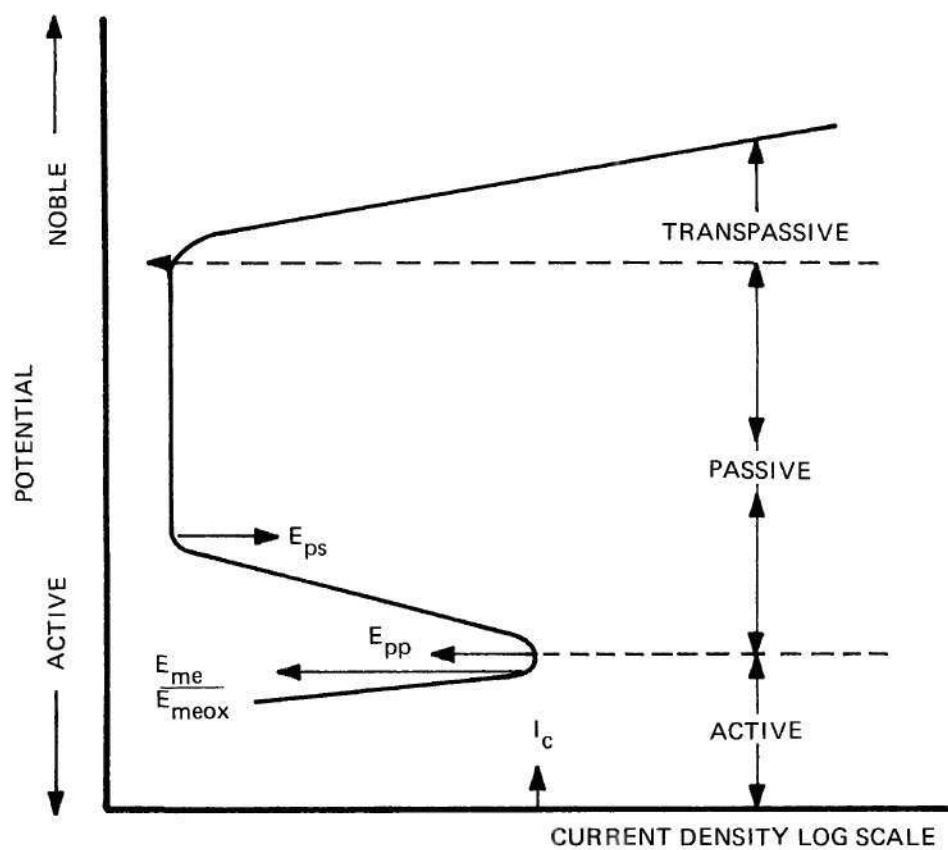
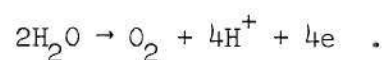


Figure 6. Schematic Anodic Dissolution Behavior of a Metal Demonstrating an Active-Passive Transition. (From Greene 19 , Modified.)

The growth of the protective film inhibits the anodic process and causes the polarization curve to shift to  $E_{ps}$  which indicates that the entire surface is covered with the film and the metal is in the passive condition. In the passive condition, an increase in potential does not cause an increase in current density until the oxygen discharge potential is exceeded producing the reaction



The electrochemical dissolution of metal takes place at potentials more noble than the transpassive potential designated  $E_t$  in Figure 6.

## CHAPTER II

### EXPERIMENTAL PROCEDURE

#### Materials

The amalgam alloy powder that was used in this study is named "Optalloy" and is commercially available to dentists. The  $\text{Ag}_3\text{Sn}$  used in ingot form had a composition of approximately 73.15 weight per cent silver and 26.85 weight per cent tin. The mercury which was used was a commercial variety available to dentists on the open market. The "Optalloy",  $\text{Ag}_3\text{Sn}$  ingot, and mercury were supplied by the L. D. Caulk Co.

Reagent grade chemicals were used in preparing the synthetic saliva according to the formula of Ross (14) which was based on the average inorganic concentrations for stimulated saliva according to Jenkins (22). The saliva formula is found in Table 1. The pH of the synthetic saliva electrolyte was adjusted to 6.7 by bubbling carbon dioxide through the solution.

#### Specimen Preparation

A series of amalgam specimens were prepared with 5:5, 7:5, and 9:5 mercury to alloy ratios by weight. The proportions of alloy and mercury were weighed on an analytical balance with an accuracy of 0.001 gram. The alloy and mercury were mixed or triturated for 15 seconds in a "Wiggle Bug" mechanical amalgamator manufactured by the Crescent Dental Manufacturing Company. The amalgams were condensed into Teflon cylindrical blocks which contained an embedded nickel wire conductor because

nickel will not react with mercury in the temperature range of this study. The blocks served as holders for the test specimens with a surface area of one square centimeter. The amalgams were allowed to set for one week before the surface was polished. Amalgam is completely hardened or reacted after one week which more nearly simulates the time at which a dentist would polish an amalgam after its insertion. Test specimens were initially ground on water lubricated metallographic silicon carbide papers from 240 grit through 600 grit. The specimens were finally polished on a lap wheel using successively finer diamond paste through a range of sizes from 6 to 0.25 microns with methyl alcohol serving as the solvent. After polishing, the specimens were rinsed in running water and then successively dipped in benzene and methyl alcohol. Next, they were rinsed in running distilled water and dried in a stream of purified nitrogen.

Table 1. Composition of Synthetic Saliva Solution

Component		Weight (Gm)
Dipotassium Hydrogen Phosphate	$K_2HPO_4$	0.200
Calcium Phosphate	$Ca_3(PO_4)_2$	0.300
Potassium Thiocyanate	KSCN	0.330
Sodium Bicarbonate	$NaHCO_3$	1.500
Sodium Chloride	NaCl	0.700
Potassium Chloride	KCl	1.200
Urea	$(NH_2)_2CO$	0.130
Distilled water added to make one liter.		

The small crevice between the test specimen and the Teflon specimen holder was sealed by applying an alkyd varnish with a small camel hair brush.

The  $\text{Ag}_3\text{Sn}$  specimens were machined from the ingot and forced into the Teflon specimen holders.  $\text{Ag}_3\text{Sn}$  surfaces were prepared in the same manner as the amalgam samples.

The specimen test electrodes were completed when the nickel electrical conductor was placed through the glass tube which was sealed to the Teflon block with high purity paraffin wax as is shown in Figure 7. The specimen was then placed into the corrosion cell containing 160 cc of synthetic saliva for electrochemical examination.

#### Anodic Polarization Curves

A Beckman Electroscan 30 potentiostat was used throughout this investigation for all electrochemical measurements. A Beckman saturated calomel electrode (SCE) was used as the reference electrode and it was connected to the saliva solution by means of double bridge to prevent contamination of the reference electrode. The (SCE) produces a stable potential of +0.244 volts relative to the normal hydrogen electrode (NHE). By convention, the potential of the (NHE) is taken to be zero.

A large platinum electrode was used as the working electrode. The corrosion apparatus is shown in Figure 8. A stepwise change in potential was used in obtaining the polarization curves. The potential was increased in increments of 20 millivolts after resting at each step for 2.5 minutes. The current measurements were taken after 2 minutes at each potential step. The starting potential corresponded to the rest or



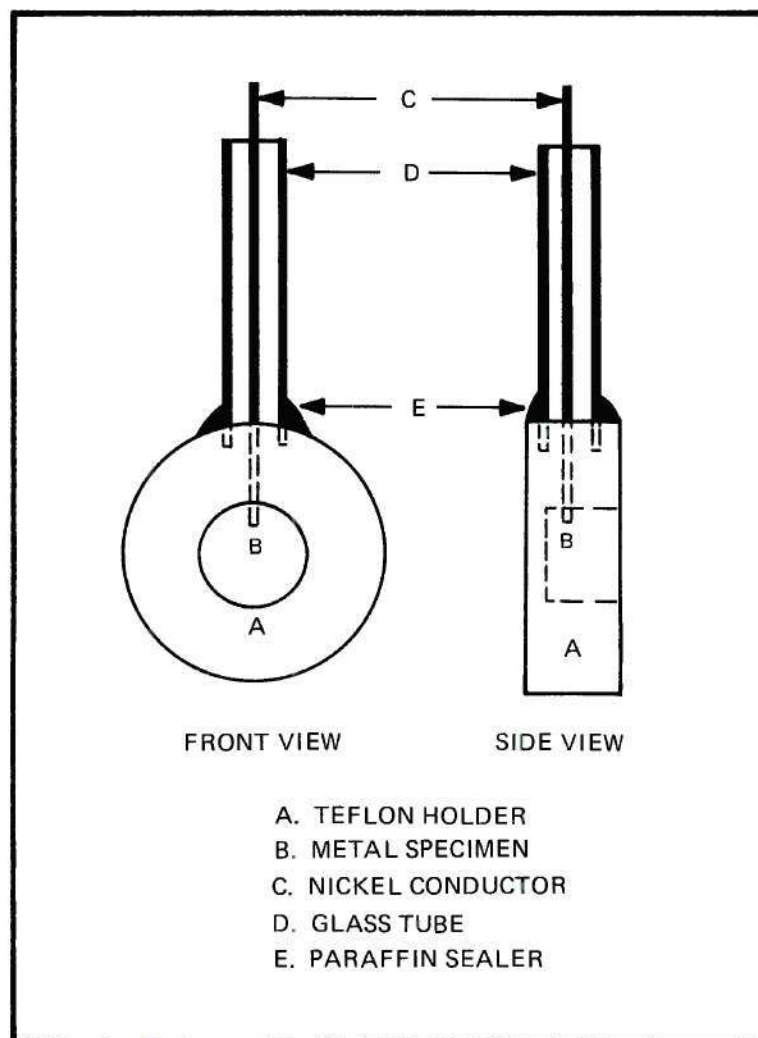


Figure 7. Drawing of the Electrode Holder for an Amalgam and Alloy.

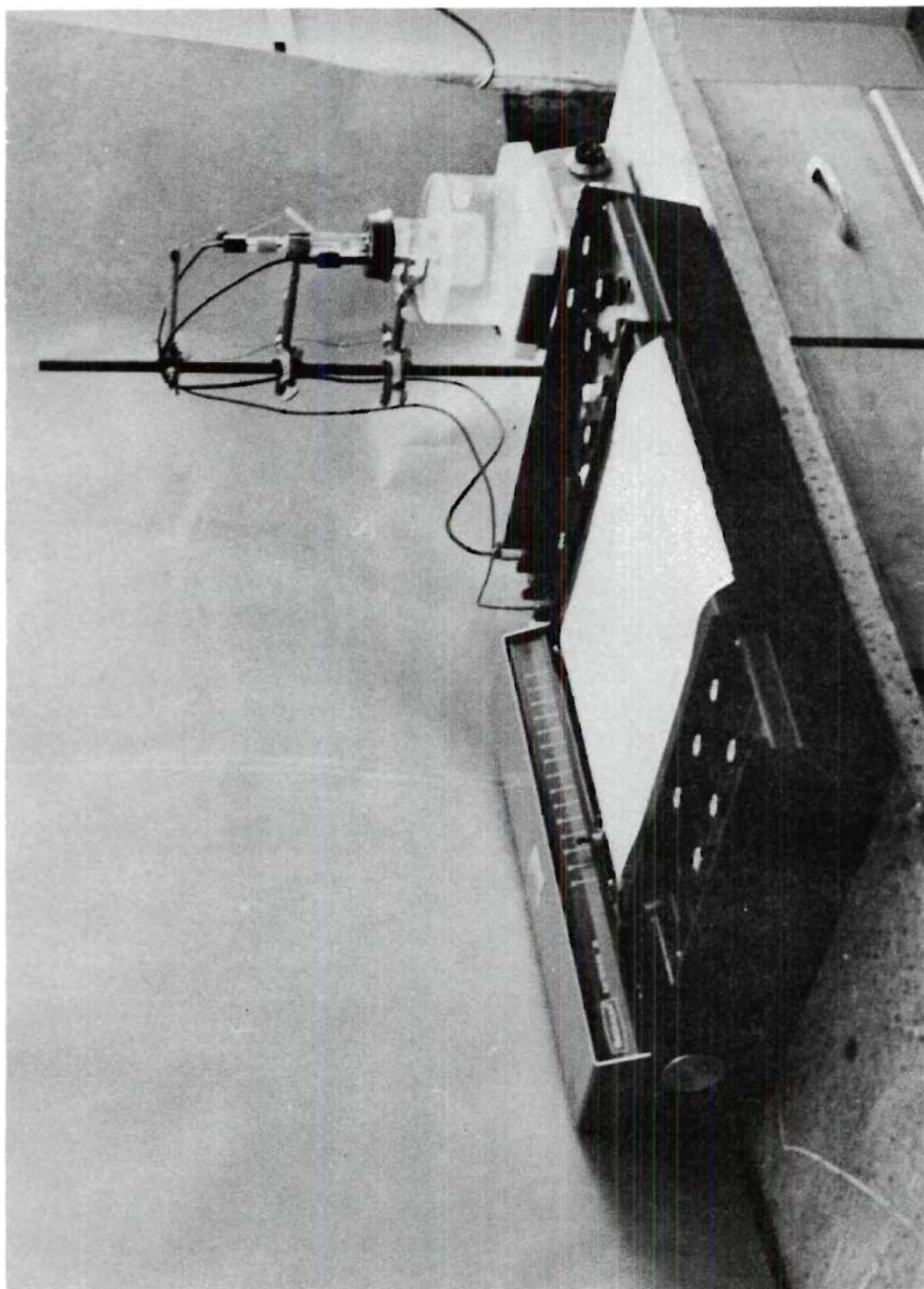


Figure 8. Potentiostat and Corrosion Cell.



open circuit potential of the specimen in the saliva solution. The samples were polarized anodically over a range of one volt. All electrochemical measurements were made in a stirred aerated solution which was maintained at 37°C to better simulate an oral environment.

Additional anodic polarization curves were obtained by the potentiodynamic method, i.e., varying the potential at a constant rate and recording the corresponding current. The potential was increased at a constant 60 millivolts per minute from the rest potential and the sample was polarized only to the point at which there was a sudden increase in current density. At this point, optical and scanning electron micrographs (SEM) were made to compare with micrographs made prior to polarization to determine the extent and location of the corrosive attack.

#### Potential-Time Curves

Corrosion potential was measured as a function of immersion time to determine the effects of the various mercury to alloy ratios on the electrochemical behavior of amalgam and  $\text{Ag}_3\text{Sn}$ . The potential was recorded for twenty-four hours after the specimen was immersed in the solution.

#### Corrosion at a Constant Potential

Amalgam specimens having mercury to alloy ratios of 5:5, 7:5, and 9:5 were polarized in the solution for 1.5 hours at a constant potential of -0.15 volts. Prior to immersion, the specimens were subjected to electron microprobe analysis for silver and tin. Optical and scanning electron photomicrographs were made before the amalgams were corroded in

order to have a basis for comparison. The potential of -0.15 volts was selected because large corrosion currents had not been observed at this potential in the potentiostatic studies of this investigation.

After the samples were polarized, they were examined microscopically for evidence of corrosion. They again were analyzed with the electron microprobe for silver and tin. The synthetic saliva in which the amalgam had been polarized was analyzed for tin content with a Perkin Elmer Atomic Absorption Spectrophotometer.

## CHAPTER III

## DISCUSSION OF RESULTS

Anodic Polarization CurvesPotentiostatic Method

The effects of mercury to alloy ratio on the potentiostatic polarization of dental amalgam and  $\text{Ag}_3\text{Sn}$  in synthetic saliva are shown in Figure 9. Polarization curves were obtained on five specimens of each type. All of the curves were in good agreement. The open circuit potentials of the various alloys are listed in Table 2 and the standard electrode potentials of the constituent elements are given in Table 3. The amalgams, regardless of the mercury to alloy ratio, had a metal dissolution peak which reached a maximum at a potential of  $+0.09 \pm 0.05$  volts. The rate of metal dissolution decreased with potential increases to approximately +0.25 volts and then the current density remained stable at  $120 \pm 10 \mu \text{ a/cm}^2$  up to approximately  $+0.10 \pm 0.02$  volts with a current density of  $60 \mu \text{ a/cm}^2$ . The current density decreased to  $25 \mu \text{ a/cm}^2$  at a potential of +0.15 volts and then proceeded to increase steadily as the potential was increased up to +0.85 volts. The potential was not increased to the point of oxygen evolution because the maximum potential recorded in vivo has been approximately 0.5 volts (1) which was exceeded in this investigation.

After the amalgams were polarized to +0.75 volts, corrosion products covered the surface. There was a loose black deposit but,

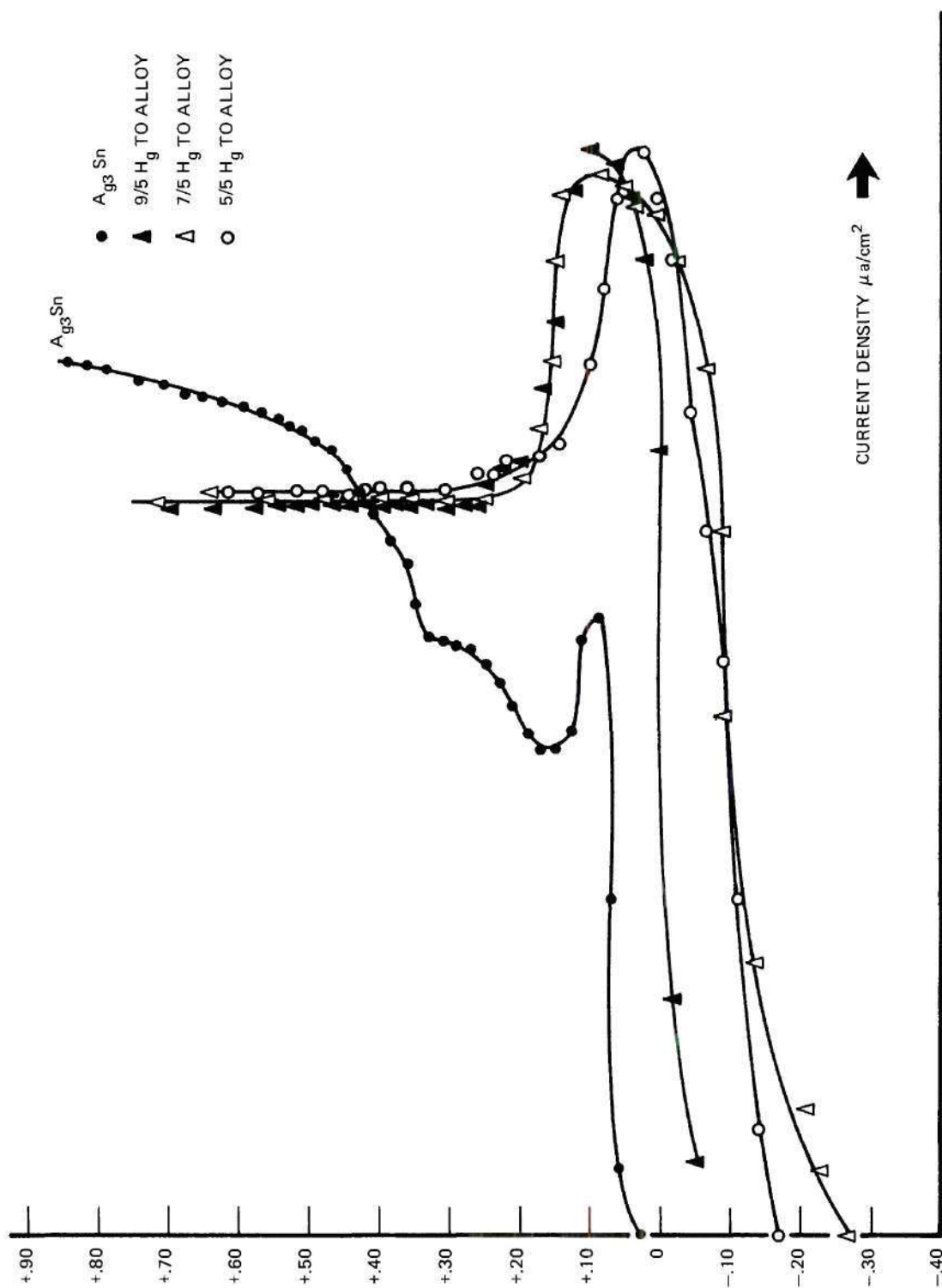


Figure 9. Anodic Potentiostatic Polarization Curves for Dental Amalgams with Mercury to Alloy Ratios of 5:5, 7:5, and 9:5 and  $\text{Ag}_3\text{Sn}$ .

Table 2. Open Circuit Potentials of Amalgam and Amalgam Alloy in Synthetic Saliva

Mercury to Alloy Ratio	Potential Relative to (SCE) Volts
9:5	$-0.45 \pm 0.02$
7:5	$-0.41 \pm 0.02$
5:5	$-0.38 \pm 0.02$
$\text{Ag}_3\text{Sn}$	$-0.25 \pm 0.01$

Table 3. Standard EMF Series of Constituent Elements Found in Dental Amalgam

Metal-Metal Ion Equilibrium (Unit Activity)	Electrode Potential Versus Normal Hydrogen Electrode at 25°C (Volts)
$\text{Ag} - \text{Ag}^+$	+0.799
$\text{Hg} - \text{Hg}_2^{+2}$	+0.788
$\text{Cu} - \text{Cu}^{+2}$	+0.337
$\text{Sn} - \text{Sn}^{+2}$	-0.136
$\text{Zn} - \text{Zn}^{+2}$	-0.763



because of the complexity of the material, no identification was made. According to Guthrow, et al., the deposit contains silver chlorides and other compounds that could not be identified using both X-ray and electron diffraction methods.

The rest potentials of the amalgams in the synthetic saliva indicate that the activity increases with an increase in mercury to alloy ratio. This indicates that the matrix is more active than the unreacted  $\text{Ag}_3\text{Sn}$  phase because the matrix volume increases if more mercury is used.

#### Potentiodynamic Method

The potentiodynamic or potentiokinetic polarization curves are shown in Figures 10 and 11. The potential was increased at a constant rate of 60 millivolts per minute which is much faster than in the potentiostatic method and the metal did not have as much time to build up a passivating layer. Therefore, the potentiodynamic curves showed different electrochemical behavior than did the potentiostatic curves.

The mercury to alloy ratio did not affect the potential at which the amalgams showed a rapid increase in current density. In all tests, the amalgams were polarized from their rest potential and showed a constant increase in current density up to a potential of  $-0.04 \pm 0.01$  volts and  $1.5 \pm 0.5 \mu \text{a/cm}^2$ . Above approximately  $-0.04$  volts, the entire surface of the specimen was covered with corrosion products. When the potential was held constant at  $+0.04$  volts, currents as high as  $1000 \mu \text{a/cm}^2$  were observed. Information regarding passivation characteristics could not be obtained at potentials higher than  $+0.04$  volts because of the rapid deterioration of the amalgam surface. A constant flow of

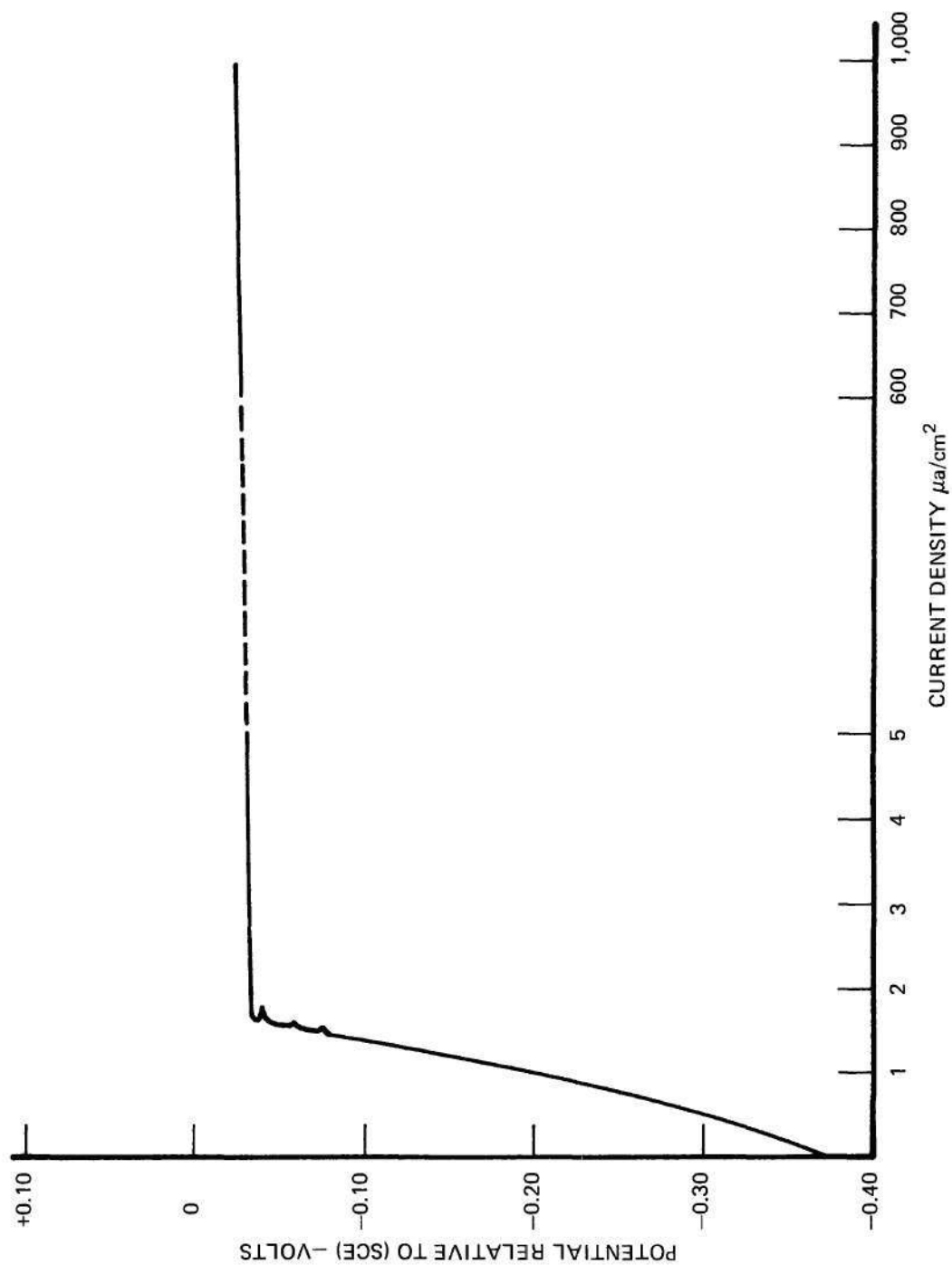


Figure 10. A Typical Anodic Potentiodynamic Polarization Curve of Dental Amalgam.



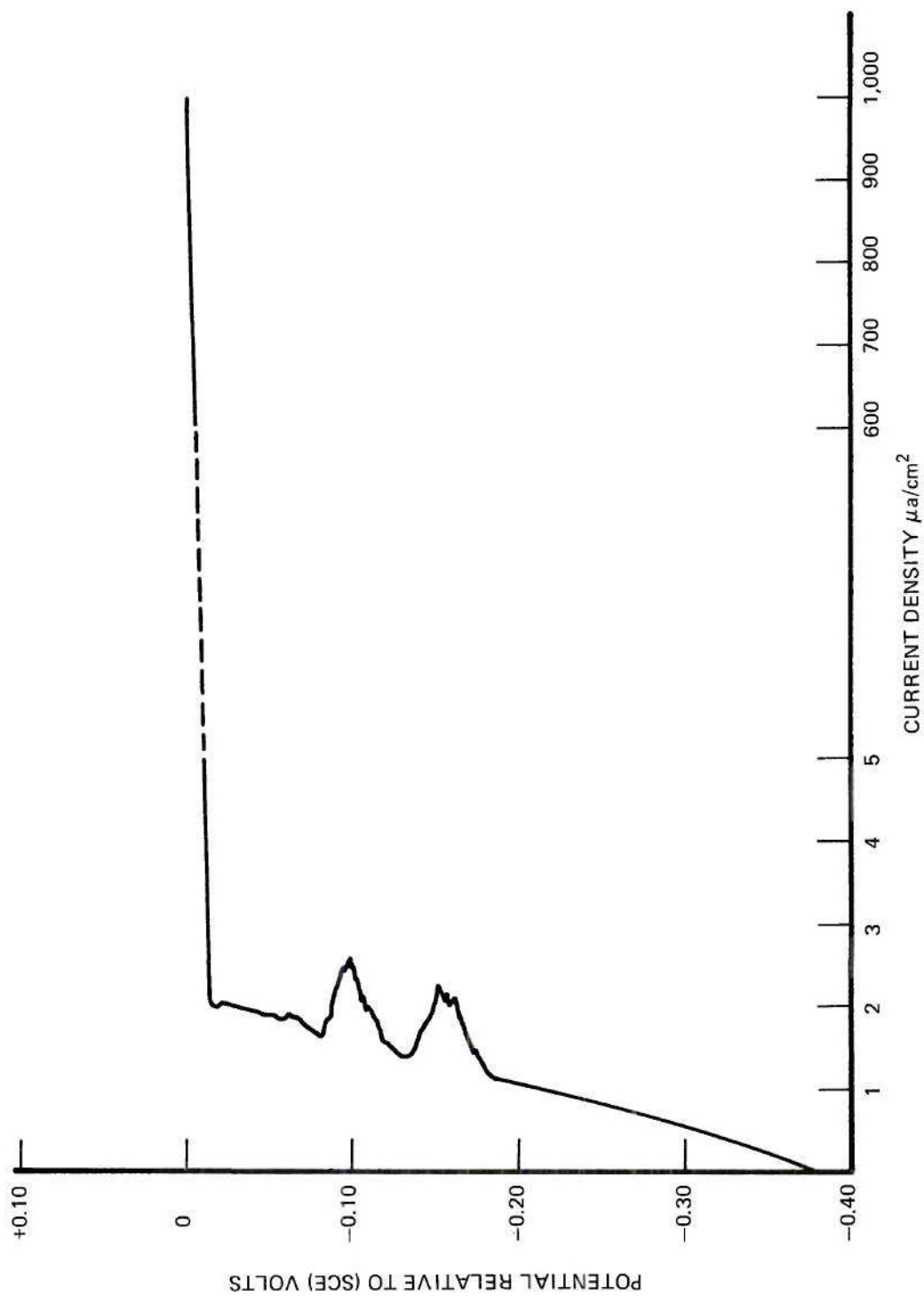


Figure 11. A Typical Anodic Potentiodynamic Polarization Curve of Dental Amalgam which Demonstrated Corrosion in Pits.

corrosion products were observed streaming from the specimen into the saliva solution at potentials greater than +0.04 volts.

The corrosion products were not generated over the entire surface with a gradual uniform build-up but had a localized point of initiation from which they spread. Figure 11 shows small peaks in corrosion rate at potentials below which gross surface corrosion occurred. Some specimens were removed after these small initial peaks for microscopic examination. The point of corrosive attack was observed to occur in small pores in the surface. All amalgam has inherent porosity and large increases in current coincided with corrosive attack in and around the microscopic pores. The pores occur mostly in the matrix phase but are also found to a limited extent in the  $\text{Ag}_3\text{Sn}$ . Corrosion in pores can be seen in Figures 12 and 13. This is analogous to crevice corrosion which is said to be responsible for the cavity sealing property of amalgam restorations (2). The potentiodynamic curves indicate that porosity or small crevices have a greater influence on corrosion than does the mercury to alloy ratio.

#### Potential Versus Time Curves

Typical curves of amalgam and  $\text{Ag}_3\text{Sn}$  showing potential as a function of immersion time are shown in Figure 14. Repeated curves were in good agreement. There was a rapid shift in potential in the noble direction with most of the shift occurring within the first six hours. The potential gradually moved in the noble direction after the first six hours and remained relatively constant at -0.20 volts after twenty-four hours. The mercury to alloy ratio did not have much effect on the shape of the

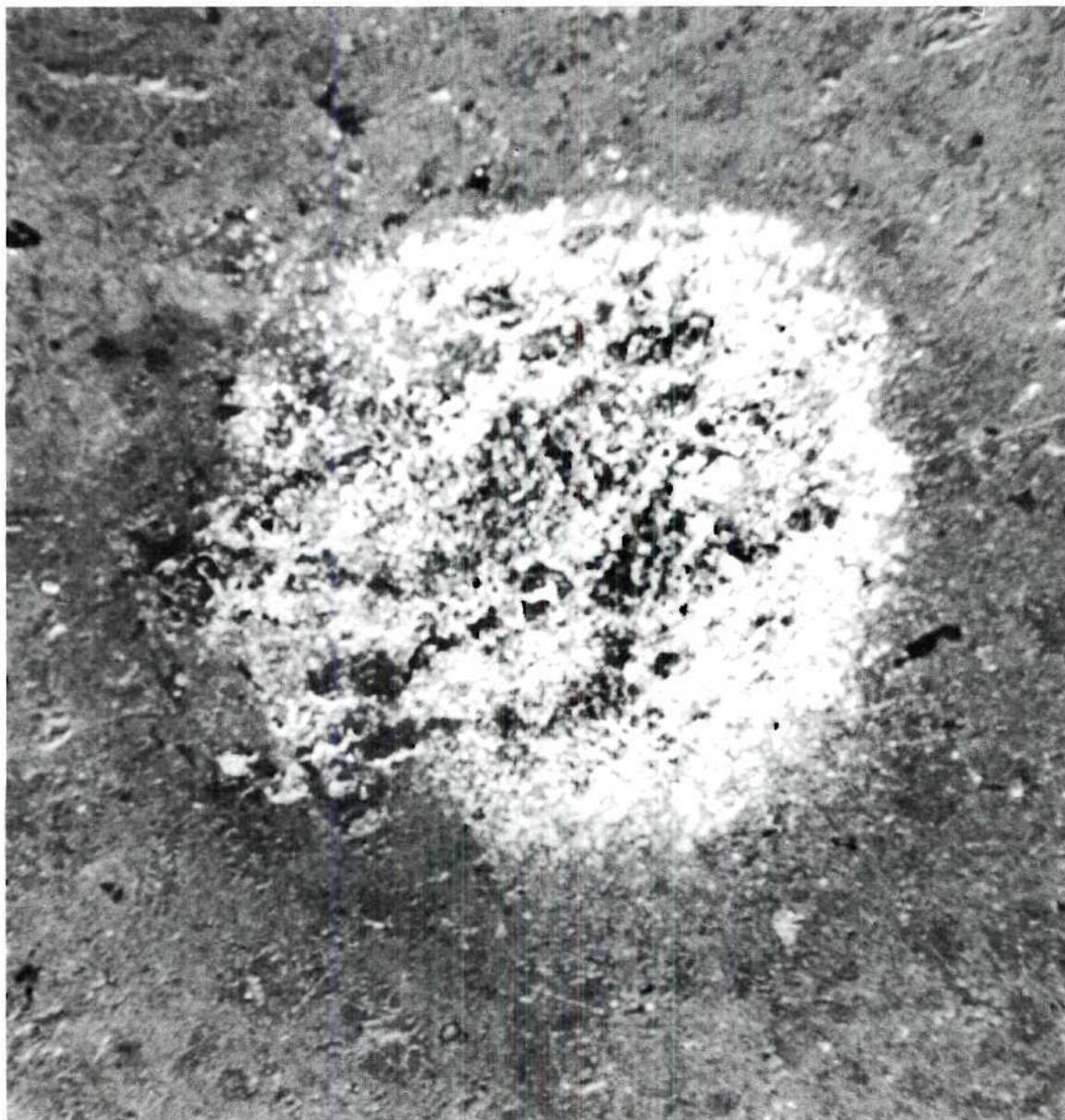


Figure 12. Corrosion of a Pit in the Surface of a Dental Amalgam (SEM) X960.



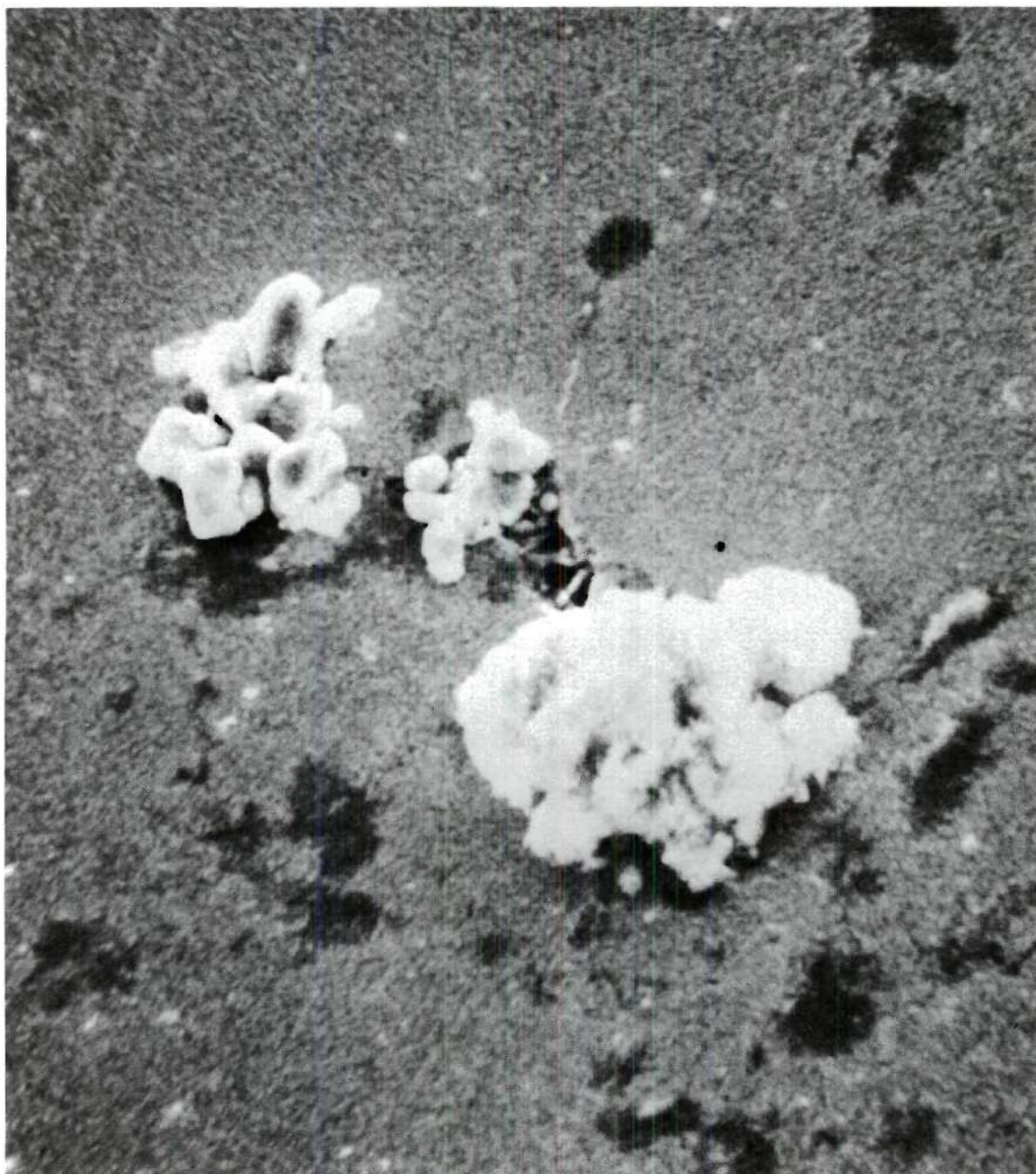


Figure 13. Corrosion of a Pit in the Surface of  $\text{Ag}_3\text{Sn}$  (SEM) X10,000.



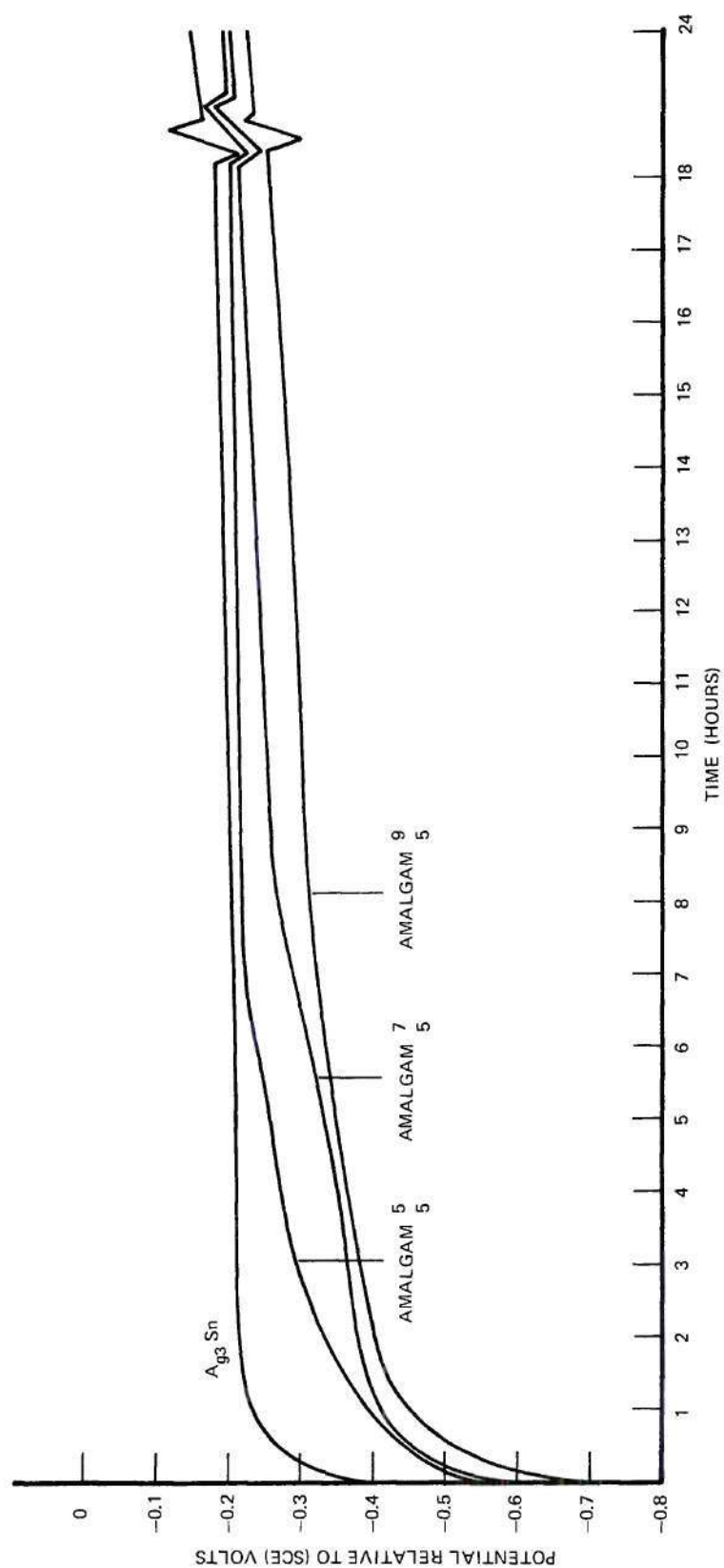


Figure 14. Potential Versus Time Curves for Dental Amalgam and  $\text{Ag}_3\text{Sn}$ .

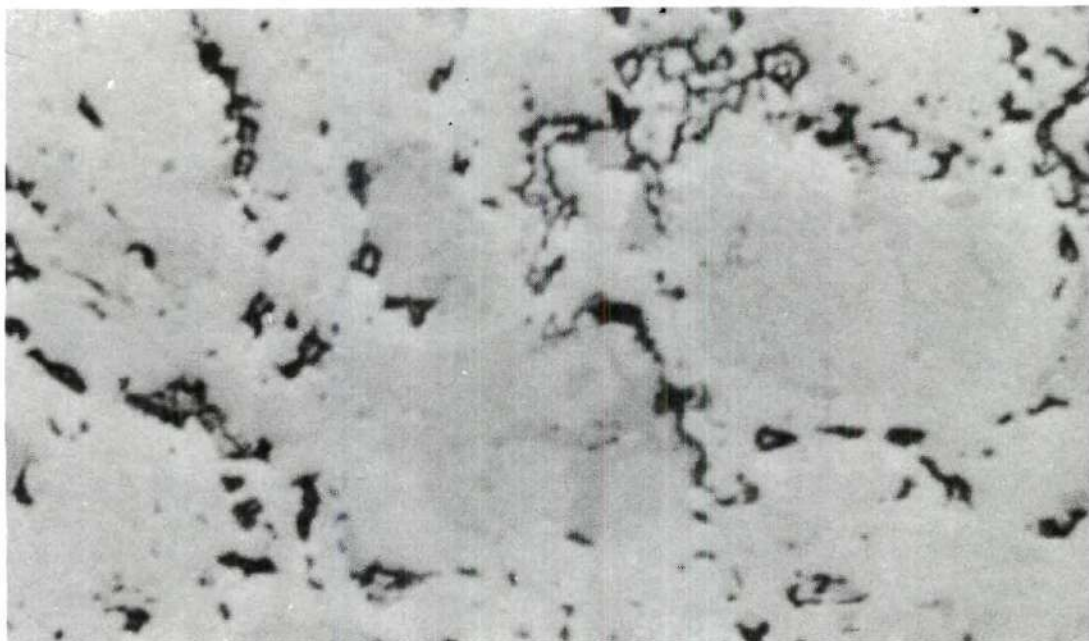
curve nor on the potential after twenty-four hours. The rapid polarization of the amalgams and  $\text{Ag}_3\text{Sn}$  in the solution indicates that some kind of oxide layer or other form of passivating film decreases the activity of the material.

### Corrosion at a Constant Potential

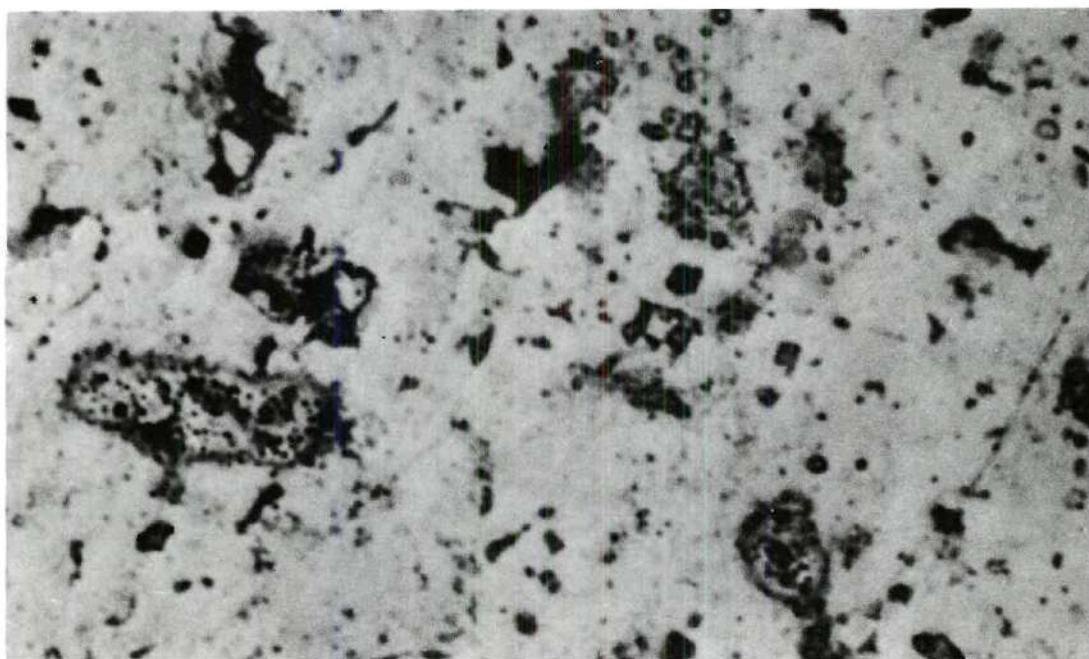
#### Optical and Electron Micrographs

Figures 15 through 17 demonstrate the effect of a constant corrosion potential of -0.15 volts for 1.5 hours on amalgam. The optical micrographs reveal no corrosion products on the amalgam surface; however, numerous small pits both in the matrix phase and in the unreacted  $\text{Ag}_3\text{Sn}$  phase were observed after polarization. The corrosion pits are smaller and more regularly shaped than the inherent porosity. The amalgams with a higher mercury to alloy ratio appeared more corroded, especially in the  $\text{Ag}_3\text{Sn}$  phase. This is an expected observation since they have a more active open circuit potential.

Figure 18 and 19 show typical scanning electron micrographs of amalgam before and after corrosion at a potential of -0.15 volts for 1.5 hours. At high magnification, no distinction could be made between the various mercury to alloy ratios studied. The unreacted  $\text{Ag}_3\text{Sn}$  particles reflect electrons differently than the matrix phase and are easily distinguishable. There appeared to be some type of deposit on the  $\text{Ag}_3\text{Sn}$  particles after corrosion. The deposit did not have the fluffy appearance of the corrosion products which were observed in the pores in the potentiodynamic studies. The deposit preferred to collect in the small scratches on the  $\text{Ag}_3\text{Sn}$  particles.



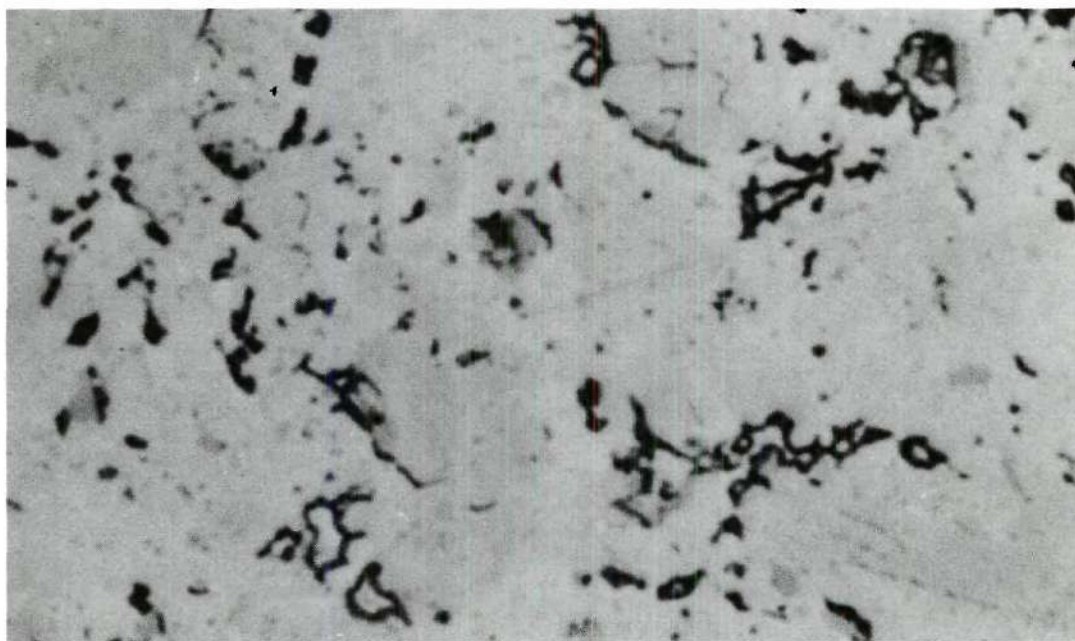
(a)



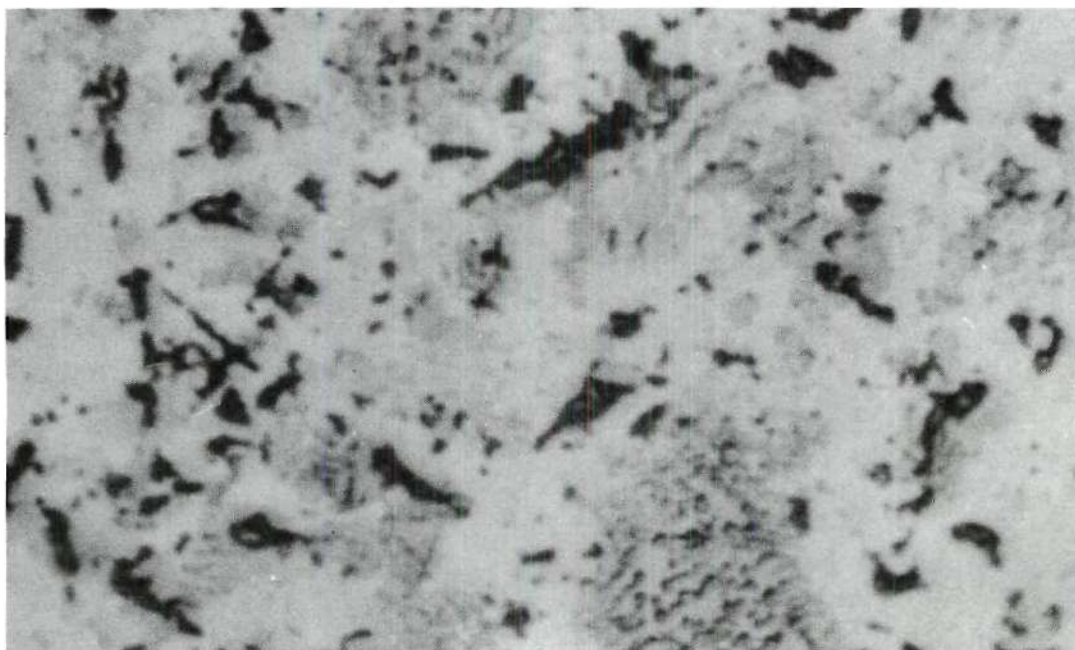
(b)

Figure 15. Optical Micrographs of Amalgam with a 5:5 Mercury to Alloy Ratio: (a) Before Polarization, (b) After Polarization for 1.5 Hours at a Potential of -0.15 Volts Relative to (SCE) X1,600.





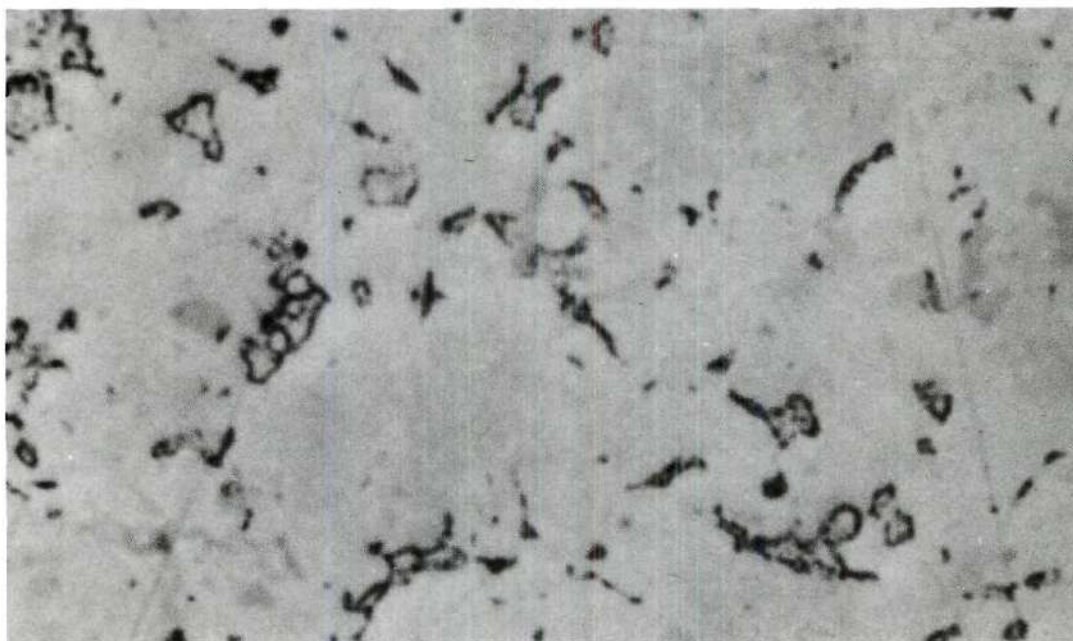
(a)



(b)

Figure 16. Optical Micrographs of Amalgam with a 7:5 Mercury to Alloy Ratio: (a) Before Polarization, (b) After Polarization for 1.5 hours at a Potential of  $-0.15$  Volts Relative to (SCE) X1,600.





(a)

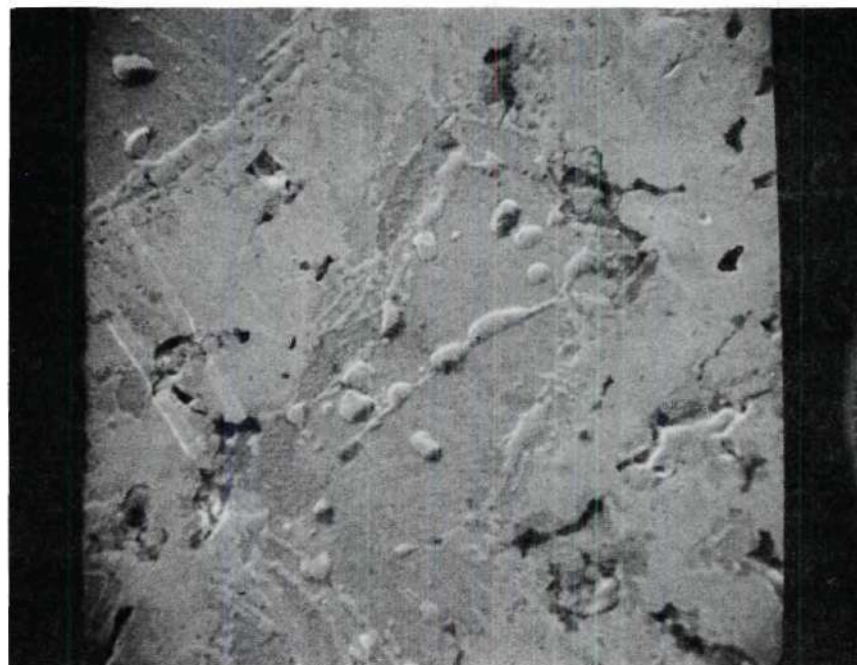


(b)

Figure 17. Optical Micrographs of Amalgam with a 9:5 Mercury to Alloy Ratio: (a) Before Polarization, (b) After Polarization for 1.5 Hours at a Potential of -0.15 Volts Relative to (SCE) X1,600.



(a)



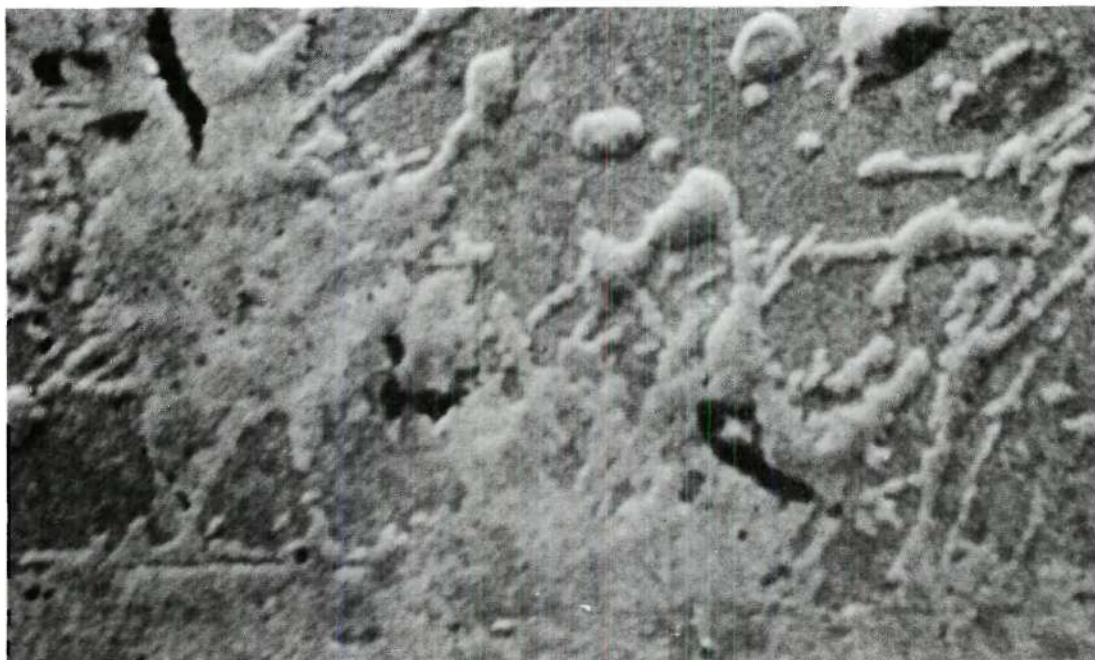
(b)

Figure 18. Typical Scanning Electron Micrographs of Dental Amalgam: (a) Before Polarization, (b) After Polarization for 1.5 Hours at a Potential of -0.15 Volts Relative to (SCE) X2,500.





(a)



(b)

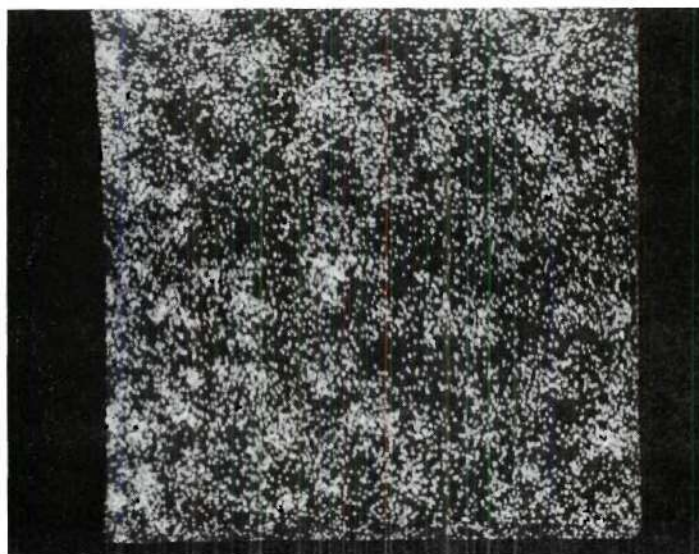
Figure 19. Typical Scanning Electron Micrographs of Dental Amalgam: (a) Before Polarization, (b) After Polarization for 1.5 Hours at a Potential of -0.15 Volts Relative to (SCE) X10,000.

#### Electron Probe X-Ray Microanalysis

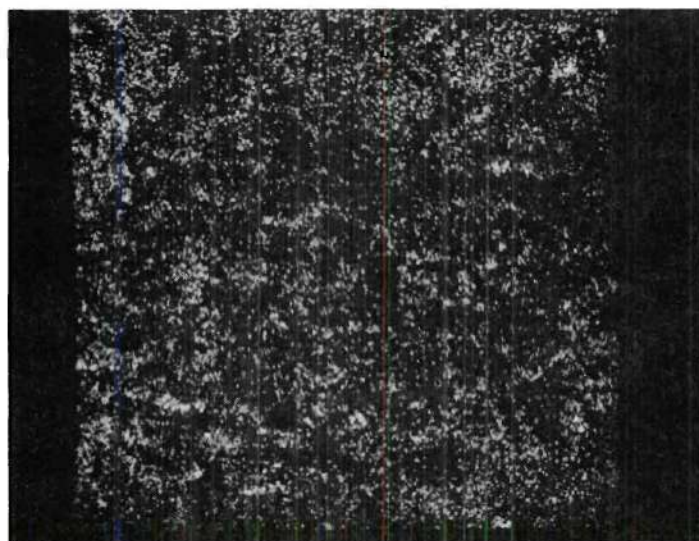
Only qualitative information was obtained with the electron microprobe. In all amalgams analyzed, the percentage of tin in the surface was reduced after the amalgams had been polarized at -0.15 volts for 1.5 hours and the silver content had increased. This definitely indicates that tin is corroded preferentially to silver. Figures 20 and 21 show typical silver and tin distributions before and after corrosion.

#### Atomic Absorption Spectrophotometry

The synthetic saliva solution in which the amalgams had been polarized for 1.5 hours at a potential of -0.15 volts was analyzed with the spectrophotometer for tin ions and none were detected in the initial series of tests. The tin ion activity was suspected of being reduced by complexing agents in the solution and perchloric acid was added to ionize the tin. The solutions were again analyzed and tin was detected in amounts of approximately 1 ppm. No appreciable difference in tin content of the solutions from amalgams with varying mercury to alloy ratios was detected because concentrations in the magnitude of 1 ppm approaches the lower limits of resolution of the instrument.



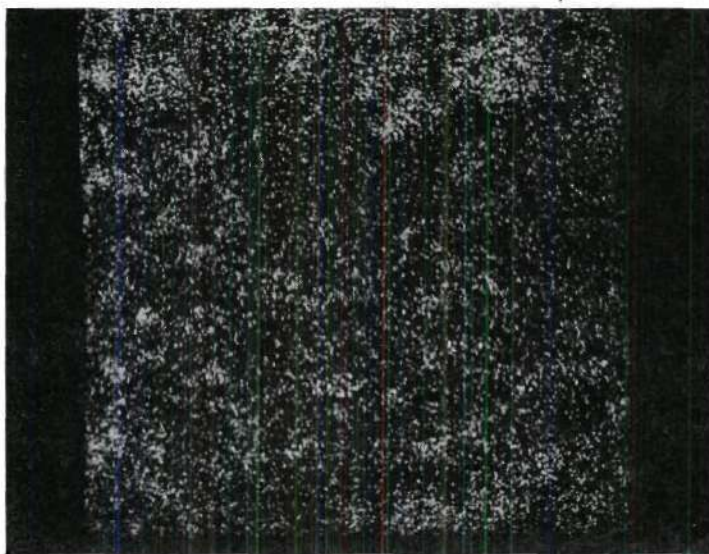
(a)



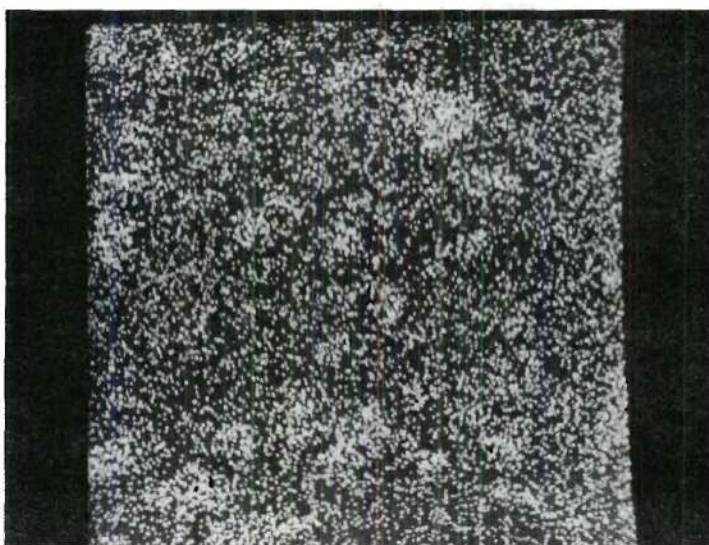
(b)

Figure 20. X-Ray Scan Micrographs Showing the Tin Distribution in Amalgam:  
(a) Before Polarization, (b) After Polarization at  $-0.15$  Volts for  
1.5 Hours.





(a)



(b)

Figure 21. X-Ray Scan Micrographs Showing the Silver Distribution: (a) Before Polarization (b) After Polarization at  $-0.15$  Volts for 1.5 Hours.

## CHAPTER IV

## CONCLUSIONS

1. Dental amalgam exhibits in this synthetic saliva used in this study dissolution peaks which occur at potentials between +0.03 volts and +0.10 volts relative to (SCE). The maximum current density of the peaks was  $1300 \mu \text{ a/cm}^2$ .

2. Surface pores were the sites of initial film formation. The film spreads from the pores to cover the surface. This indicates the corrosion behavior of amalgam is sensitive to a change in environment provided by surface defects such as microscopic pits and crevices.

3. This investigation and the in situ corrosion characteristics of dental amalgam indicate that its corrosion resistance is not due to an active-passive transformation. High circuit resistance in an oral environment and amalgam being a relatively noble material are factors contributing to its corrosion resistance.

4. Tin corroded preferentially to silver and tin ions were reduced by complexing agents in the synthetic saliva solution.

## CHAPTER V

## RECOMMENDATIONS

1. Identify the film which causes passivation in the potential versus time curves.
2. Employ ultrasonic energy to seal the pits and investigate changes in corrosion characteristics.
3. Determine the corrosion current as a function of matrix area.
4. Pits change pH and localized corrosion begins. Relate this to the corrosion at the crevice interface.

## APPENDIX

## ELECTROANALYTICAL SYSTEM (23)

All electrometric techniques in this investigation employed the use of a potentiostat which is an electronic device that maintains a metal at a constant potential with respect to a reference electrode. The potentiostat has three electrodes as shown in Figure 22. The reference electrode (saturated calomel electrode) is in the summing loop, the working electrode (amalgam electrode) is located at point  $E_r$ , and the auxiliary electrode (platinum electrode) is in the feedback loop. The net voltage in the system is composed of three voltage sources. These are  $E_i$ , which is set at a fixed value;  $E_s$ , which can be varied linearly with time; and  $E_r$ , the reference electrode voltage. An external voltage,  $E_{ex}$ , can also be applied. These voltages,  $E_i$ ,  $E_s$ ,  $E_r$ , and  $E_{ex}$  are additive in the summing loop.

In operation, the selected voltage is sensed at the summing point of the amplifier. The amplifier then generates current in the feedback loop through the cell by means of the working and auxiliary electrodes so the voltage at the working electrode surface is equal and opposite to the selected voltage. Thus, the potential at the surface of the working electrode is selected and is controlled by the amplifier system independent of cell resistance provided the voltage drop does not exceed the power capabilities of the amplifier. The current through the recorder resistor  $R_r$ , produces a voltage proportional to the current which is read out on the recorder.

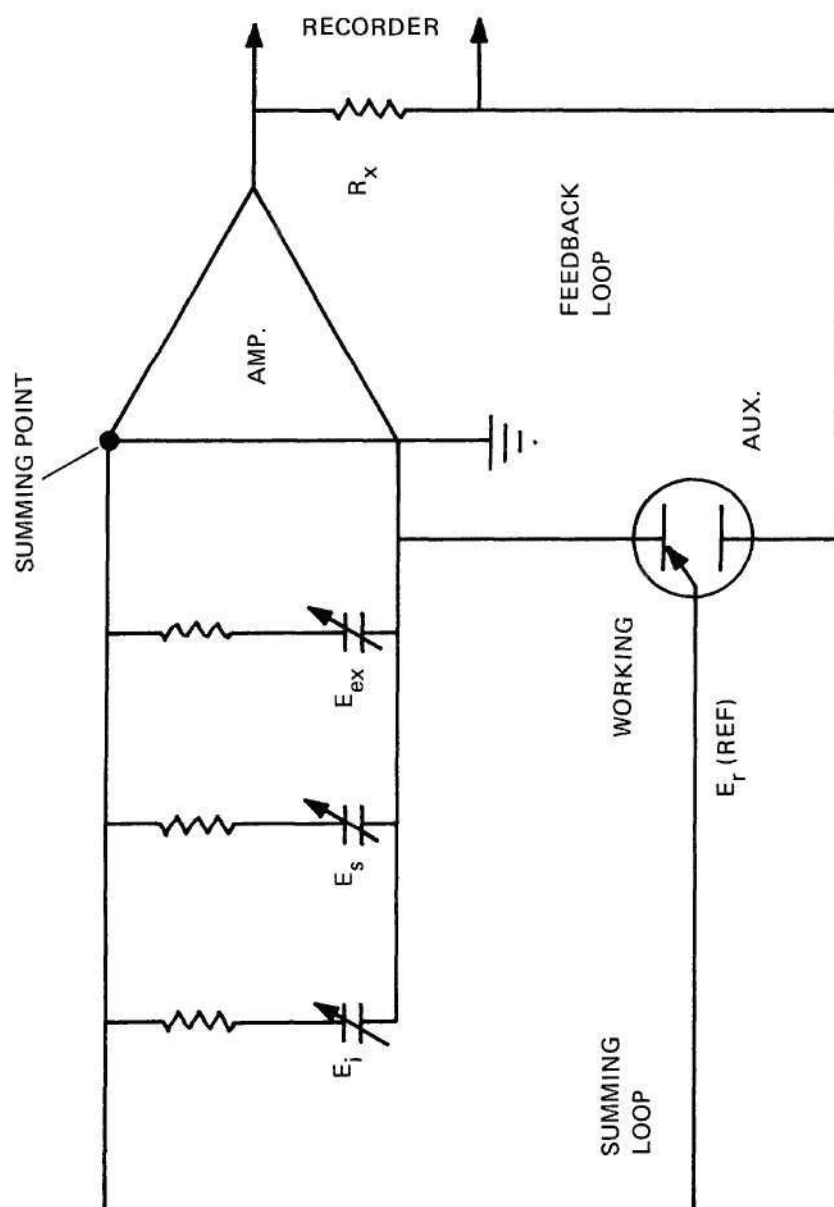


Figure 22. A Simplified Diagram of the Potentiostatic Circuit.



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